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13. SUPPLEMENTARY NOTES

14. ABSTRACT
The research described in this Final Report was directed toward measuring the time for energy flow within isolated molecules and in molecules in solution. The approach was to use a 100-fs pulse of light from a Ti:sapphire laser to pump two optical parametric amplifiers in order to generate infrared pulses, for exciting vibrations, and ultraviolet light, for exciting electronic transitons. In the gas phase experiments, one pulse excited the first overtone of the O-H stretching vibration in nitric acid and the second pulse probed the excited molecule by excitation to a dissociative electronic surface, which led to the production of electronically excited products that emitted light. The experiment showed that the flow of energy out of the O-H stretch takes about 12 ps. In the liquid experiments, the infrared pulse excited the first overtone of the C-H stretch in methylene iodide and the ultraviolet pulse probed the molecule by transient absorption. The flow of energy with in the molecule took about 10 ps, and the flow of energy into the solvent took between 70 ps (in carbon tetrachloride) and 30 ps (in benzene) depending on the solvent.

15. SUBJECT TERMS

lasers, liquids, energy transfer, intramolecular relaxation, intermolecular relaxation, ultrafast laser, vibrations

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Final Report

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Intramolecular Vibrational Energy Transfer

and

Bond-Selected Photochemistry in Liquids

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OBJECTIVES

The goal of this research is to study the behavior of vibrationally excited molecules in liquids. The experiments are designed to discover the effects of solvent and vibrational excitation level on the pathways and rates of intramolecular energy redistribution for molecules in a liquid and to use vibrational excitation to control photochemical pathways in solution.

ACCOMPLISHMENTS

Our goals during the period of AFOSR support were time-resolved observation of intramolecular energy flow in an isolated vibrationally excited molecule and extension of that approach into liquids. Our most important result is the direct observation of energy flow within a vibrationally excited molecule and into several different solvents. Our studies of vibrational energy transfer and photodissociation in liquids have required that we develop not only the ultrafast laser capability for exciting molecules vibrationally and probing their evolution but also ancillary capabilities for identifying photoproducts in solution.

Preparation and Interrogation of Vibrationally Excited Molecules

Our experimental target is the preparation and interrogation of vibrationally excited molecules during energy transfer and photodissociation. Because typical intramolecular vibrational energy transfer times are roughly 1 to 20 ps, laser pulses of about 100 fs serve our purposes well. Excitation of fundamental and first overtone vibrations require wavelengths in the range of about 1 to 4 μm while excitation of electronic transitions requires wavelengths as short as 230 nm. Modern ultrafast technology using a Ti:sapphire laser to generate 800-nm pulses and various nonlinear optical schemes to generate other wavelengths meets all of these requirements.

We have developed the ability to generate 100-fs duration pulses from a regeneratively amplified Ti:sapphire laser that produces roughly 1-mJ pulses of 800-nm light using chirped pulse amplification at 1 kHz. We have modified the commercial oscillator (Clark-MXR) with a shorter crystal to obtain more stable operation, have constructed and used white-light seeded optical parametric amplifiers based on β-barium borate to generate infrared light in the range of 1.2 to 2.7 μm, and have used frequency doubling and mixing schemes to cover the region down to 230 nm. These devices work well and are the heart of the apparatus used in the experiments described below. The apparatus also has a frequency resolved optical gating device for diagnostics along with delay lines and sample

handling capabilities. We have a proven apparatus for preparing vibrationally excited molecules in liquids and probing their electronic absorption during the course of energy flow and relaxation.

Energy Flow in Isolated Molecules

The first use of our apparatus to observe intramolecular energy flow was a measurement on gas phase nitric acid molecules in which we used a 100-fs pulse of 1.4-μm radiation to excite two quanta of O-H stretch and another pulse of 266-nm radiation to photodissociate the vibrationally excited molecules, $HONO_2(2\nu_{OH}) + h\nu \rightarrow OH + NO_2$. Some of the NO_2 products are born in an electronically excited
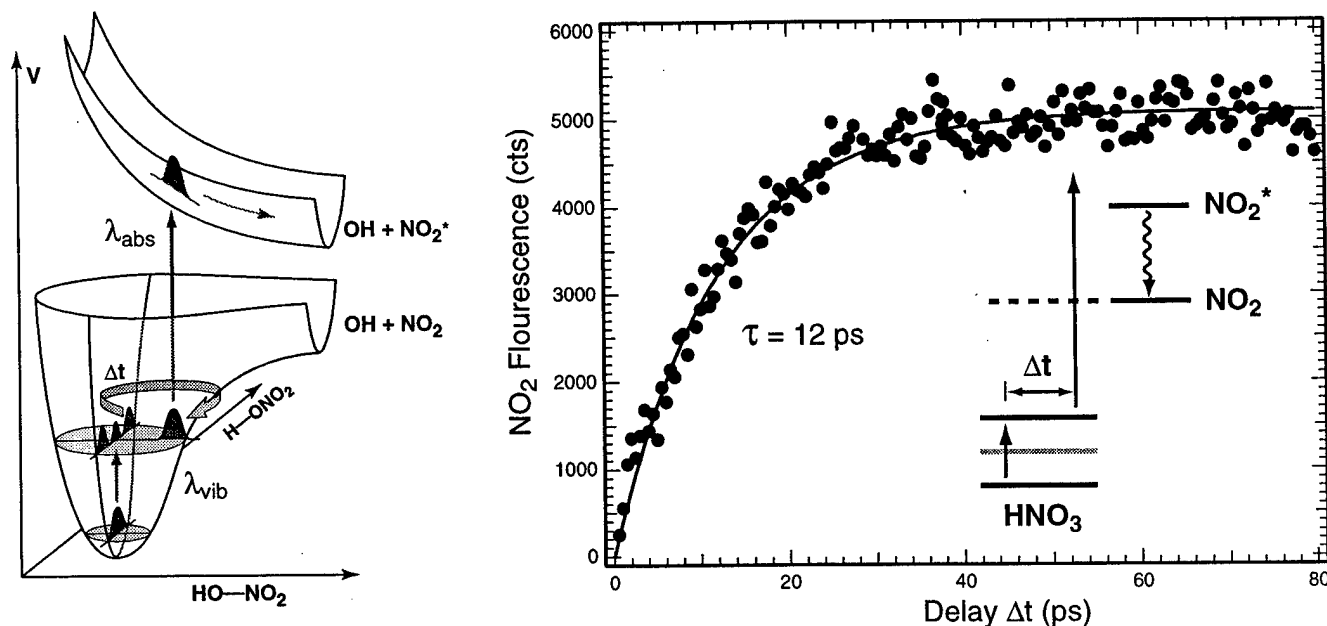

Figure 1

state and emit light. We detect the emission while varying the delay, Δt, between the vibrational over-tone excitation pulse and the dissociation pulse. As the schematic potential energy surface in Figure 1 indicates, the dissociation is much more efficient after energy flows out of the O-H stretch and into other modes of the molecule, many of which have better Franck-Condon factors for excitation to the electronically excited state. For example, stretching the HO-NO_2 bond is likely to improve the overlap along the dissociation coordinate, and bending is likely to improve the overlap with the distorted electronically excited state. Thus, the time evolution in the Figure, in which the NO_2 production grows with a characteristic time of τ=12 ps, reflects the flow of energy out of the initially excited O-H stretching vibration into other parts of the molecule. A simple Golden Rule calculation using the measured lifetime and the calculated density of states gives a coupling matrix element of about 0.08 cm^{-1} that is consistent with higher order, nonspecific coupling of the initial state to nearby vibrational

states in which several quanta of stretching and bending vibration replace one quantum of O-H stretching excitation. The measured 12-ps rise of the signal is the time for intramolecular vibrational energy distribution in the isolated molecule.

The most important aspect of the measurement on nitric acid, in the present context, is the illustration it provides of using electronic excitation to monitor the distribution of vibrational excitation in a molecule. If one knows that certain initially unexcited vibrational motions promote efficient excitation to an electronic state, transitions to that excited state, here monitored by the appearance of the emitting product, reveal the flow of energy into initially unexcited vibrations. Because the molecules are isolated, the signal increases to a constant level with the energized molecule surviving until a collision relaxes it or it leaves the observation volume. The scheme we have used for observing energy flow in isolated nitric acid molecules is the basis for our newest observations on energy flow in vibrationally excited molecules in liquids. The principle is exactly the same in our studies of liquids. We excite a molecule vibrationally and probe its energy distribution by electronic excitation, but the interaction of the excited molecules with the solvent adds a new dimension.

Intramolecular Energy Flow and Vibrational Relaxation in Liquids

Our experiments that observe the flow of energy among the vibrations of a molecule and into the solvent rest on the idea of probing vibrational energy content by transient absorption on an electronic transition. The concept comes from our earlier studies of vibrationally mediated photodissociation through molecular eigenstates, in which we projected the initial vibrational excitation in the ground electronic state onto the excited electronic state to alter the photodissociation dynamics. In the energy flow experiments, we reverse the process, using excitation to the excited electronic state to look back into the vibrational dynamics in the ground electronic state. The condensed phase experiments prepare two quanta of the stretching vibration of a bond to a light atom, just as in the measurements on isolated molecules, and again rely on a transition to an electronically excited state for interrogation. However, one dramatic difference between the measurements in liquids and those in gases is the substantially larger concentration of molecules in solution. Because even a 0.1% solution contains has about 10^{19} solute molecules in a cm^3, we are able to monitor the transition to the electronically excited state by time-resolved absorption spectroscopy, detecting the absorption of a photon rather than the subsequent appearance of a decomposition product.

Figure 2 shows the schematic potential energy surface and time evolution we measured in our first liquid phase vibrational energy transfer experiment. A 1.7-μm, 100-fs pulse of near infrared light (λ_{vib}) from one of our optical parametric amplifiers (OPA) excites two quanta of C-H stretching vibration of methylene iodide molecules (CH_2I_2) in solution. The initially prepared non-stationary
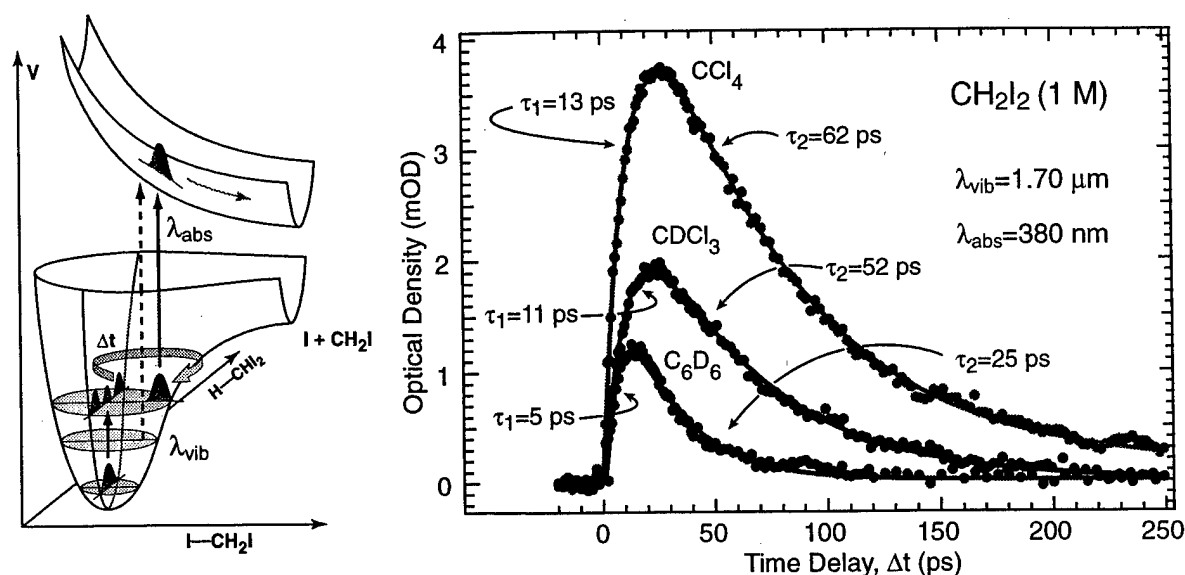
Figure 2

state evolves, transferring energy into other vibrations such as motion along the C-I stretching coordinate. Immediately after the vibrational excitation, the electronic transition probability is unchanged since the C-H stretching potential is essentially identical in the ground and excited electronic states. However, as energy flows into the other coordinates, particularly the C-I stretch, the electronic transition probability grows because the C-I stretching vibration has a better Franck-Condon factor for the transition, denoted by λ_{abs} in the Figure, to the dissociative excited state surface. As in the case of isolated nitric acid molecules, the rise in the signal reflects the time for intramolecular energy redistribution in the vibrationally excited CH_2I_2 molecules. The striking difference from the gas-phase measurement, however, is the decay of the signal. The rapid relaxation of the vibrationally excited molecules with a time constant ranging from 25 to 62 ps in different solutions is a clear manifestation of the vibrationally excited molecule being embedded in a solvent. The simplest interpretation of the growth and decay of the signal is that it arises from *intramolecular* vibrational energy transfer within the molecule, during which energy flows out of the initially excited vibration into other vibrations, followed by *intermolecular* vibrational relaxation, in which energy flows from the energized molecule into the solvent. Two variables available for testing the simple picture of intramolecular vibrational energy redistribution followed by relaxation into the solvent are the probe wavelength, which allows interrogation of different regions of the ground state potential, and the identity of the solvent, which allows exploration of different interactions between the vibrationally excited molecule and its surroundings.

The decay time for the sequential kinetics fits shown in Figure 2 depends strongly on the probe wavelength, increasing from about 30 ps to over 70 ps for CH_2I_2 in CCl_4 as the probe wavelength decreases from 440 nm to 370 nm. A *qualitative* explanation of this trend lies in the ability of more energetic probe photons to interrogate lower energy regions of the ground state potential energy surface. The solid arrow in the sketch on the left in Figure 2 shows a transition to the excited state from the initially prepared energy level after migration of the initial C-H stretching energy into other
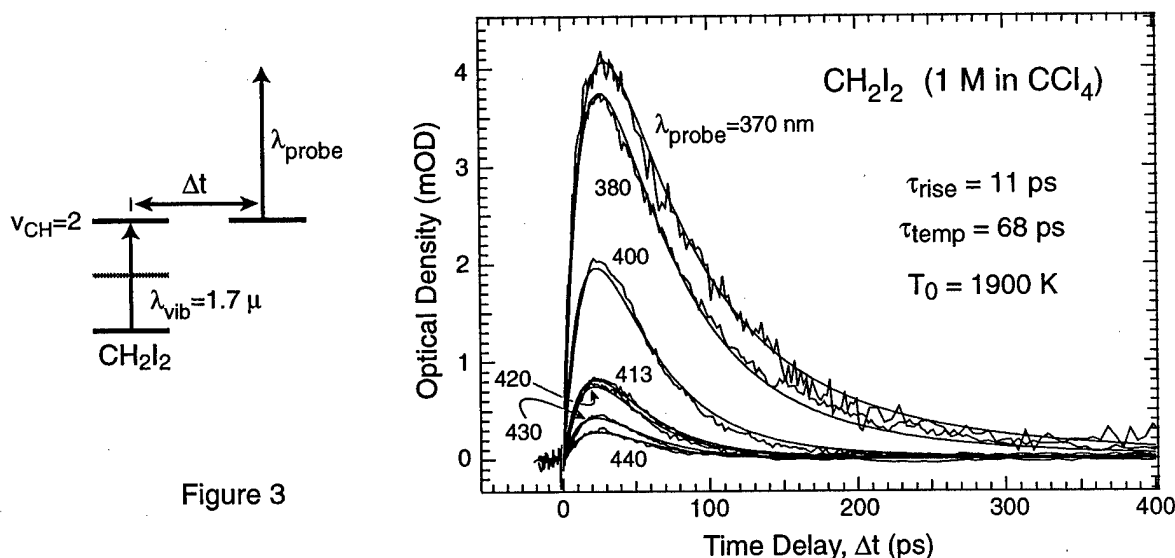

Figure 3

motions while the molecule retains its initial total energy. As energy flows from the excited molecule into the solvent, a transition to the electronically excited surface requires an increasingly energetic photon, shown as the dashed arrow in the figure. Conversely, more energetic photons interrogate lower energy molecules, and it takes longer for the vibrationally excited molecules to lose enough energy to the solvent to fall below the minimum detectable internal energy. Consequently, the phenomenological decay time depends strongly on the probe wavelength. A simple *quantitative* model recovers this behavior as well. We have measured the long wavelength portion of the absorption spectrum of CH_2I_2 in C_6D_6 at temperatures between 275 and 320 K as a means of estimating the absorption spectra of CH_2I_2 at different total energies. (This step amounts to equating the energy distribution for individual oscillators in microcanonical and canonical ensembles of molecules, an assumption that is rather good for a molecule with a large density of states. The absorption spectra are similar for all three solvents.) Using these spectra as a basis, we are able to fit data over the entire range of probe wavelengths with a temperature T_0 that characterizes the initial energy content, a single decay time τ_{temp} that describes the decay of the temperature as energy flows into the solvent, and a

single rise time τ_{rise} that characterizes the intramolecular energy redistribution. Figure 3 shows the measured curves and the fit of this model along with the three parameters for relaxation of CH_2I_2 in CCl_4. This very simple model reproduces the essential features, supporting our qualitative explanation of the probe wavelength dependence of the signal and giving times of 11 ps for intramolecular energy redistribution and 68 ps for vibrational relaxation into the solvent, values consistent with measurements on comparable systems.

The dependence of the relaxation time on solvent is interesting as well. As Figure 2 shows, the rise and decay times do not change much in going between the solvents CCl_4 and $CDCl_3$, a result consistent with there being only small differences in the interaction of the initially excited CH_2I_2 with those two solvent molecules. (We choose all of our solvents to have no vibrations lying close in frequency to the initially excited C-H stretching vibration.) The situation is very different for perdeuterobenzene (C_6D_6), where both the rise and decay of the signal are about a factor of two shorter than in CCl_4 and $CDCl_3$. We suspect that the sizeable difference reflects a stronger interaction between the solvent and solute, possibly a charge transfer interaction between the iodine atom and the benzene ring. Models that relate the rate of energy transfer to the width of vibrational transitions of the solute molecule in the different solvents do not explain our observations since the first overtone transition of methylene iodide is essentially identical in all three solvents. The strong solvent dependence of the rise and decay points to the sensitivity of both the intramolecular and intermolecular dynamics to the environment and suggests that the solvent identity is an important parameter in our experiments.

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AFOSR Sponsored Publications

D. Bingemann, M. P. Gorman, A. M. King, and F. F. Crim, *Time-resolved vibrationally mediated photodissociation of HNO3: Watching vibrational energy flow,* J. Chem. Phys. **107,** 661-664 (1997).

D. Bingemann, A. M. King, and F. F. Crim, *Transient electronic absorption of vibrationally excited CH_2I_2: Watching energy flow in solution,* J. Chem. Phys. **113,** 5018-5025 (2000).